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(54) **Polycarboxy/polyol fiberglass binder**

(57) Provided is a novel fiberglass binder comprising a polycarboxy polymer and a polyol. The amount of polycarboxy polymer and polyol contained in the binder is such that the ratio of equivalents of hydroxyl groups to carboxy groups is preferably in the range from from about 0.6/1 to 0.8/1. It is further preferred that the molecular weight of the polycarboxy polymer is less than 10,000, and more preferably less than 5000.

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of binder properties versus urea formaldehyde binders is presented in "Formaldehyde-Free Crosslinking Binders For Non-Wovens", Charles T. Arkins et al., TAPPI JOURNAL, Vol. 78, No. 11, pages 161-168, November 1995. The binders disclosed by the Arkins article, appear to be B-stageable as well as being able to provide physical properties similar to those of urea/formaldehyde resins. Unfortunately, urea/formaldehyde resins do not in general offer the same properties as phenol/formaldehyde resins, the most widely used fiberglass binder resins.

[0009] U.S. Patent No. 5,340,868 discloses fiberglass insulation products cured with a combination of a polycarboxy polymer, a  $\beta$ -hydroxyalkylamide, and an at least trifunctional monomeric carboxylic acid such as citric acid. The specific polycarboxy polymers disclosed are poly(acrylic acid) polymers.

[0010] U.S. Patent No. 5,318,990 discloses a fibrous glass binder which comprises a polycarboxy polymer, a monomeric trihydric alcohol and a catalyst comprising an alkali metal salt of a phosphorous-containing organic acid.

[0011] Published European Patent Application EP 0 583 086 A1 appears to provide details of polyacrylic acid binders whose cure is catalyzed by a phosphorus-containing catalyst system as discussed in the Arkins article previously cited. European Published Application EP 0 651 088 A1 contains a related disclosure pertaining to cellulosic substrate binders. The fiber-glass binders of EP '086 are partially neutralized polycarboxy polymers and hydroxyl-functional curing agents wherein the polycarboxy polymers are prepared in presence of sodium hypophosphite, incorporating the latter into the polymer structure or by incorporating sodium hypophosphite separately into the curable mixture of polycarboxy polymers to serve as the curing catalyst. Polymers of acrylic acid and maleic acid are exemplified, but appear to reduce both dry and wet tensile strength as compared to poly(acrylic acid) catalyzed with sodium hypophosphite. Higher molecular weight poly(acrylic acids) are stated to provide polymers exhibiting more complete cure. See also U.S. Patent No. 5,661,213.

[0012] Further, as Arkins indicates, the normal cure temperature of the acrylic binder resins is approximately 180°C, and a final cure does not take place without prolonged heating at this temperature or by allowing the temperature to rise to the range of 220°C to 240°C. The combination of curing temperature and cure time necessitates thermal energy requirements considerably in excess of what is normally desirable for phenol/formaldehyde resins. While it might seem that a simple increase in oven temperature could provide the additional thermal energy required, it must be remembered that in a commercial setting, the exceptionally large ovens, powerful heat supplies, and ancillary equipment must all be changed if a binder with higher thermal energy curing requirements is to be used. These changes are not minimal, and represent a considerable financial investment, in many cases requiring significant additional furnace length. Moreover, it is highly likely that for a considerable period of time at least, a variety of binder resins may be used on the same line at different times. Thus, any change made to the curing ovens must be easily reversible. Thus, poly(acrylic acid) binder systems having curing energy requirements similar to those of phenol/formaldehyde binders would be desirable.

[0013] While some polycarboxy polymers have been found useful for making fiberglass insulation products, problems have been observed in the processing of the products. Clumping or sticking of glass fibers to the inside of the forming chambers during the processing has been one major problem. As well, it is important that the final product exhibit the recovery and rigidity necessary to provide a commercially acceptable fiberglass insulation product.

[0014] Accordingly, it is an objective of the present invention to provide a non-phenol formaldehyde binder.

[0015] Yet another object of the present invention is to provide such a binder which allows one to prepare fiberglass insulation products with minimal processing difficulties.

[0016] Still another object of the present invention is to provide a fiberglass insulation product which exhibits good recovery and rigidity, and is formaldehyde-free.

[0017] These and other objects of the present invention will become apparent to the skilled artisan upon a review of the following description and the claims appended thereto.

## SUMMARY OF THE INVENTION

[0018] In accordance with the foregoing objectives, there is provided by the present invention a novel fiberglass binder. The binder of the present invention comprises a polycarboxy polymer and a polyol. It is also preferred that the binder comprises a catalyst, such as an alkaline metal salt of a phosphorus-containing organic acid.

[0019] An important aspect of the binder of the present invention is that the amount of polycarboxy polymer and polyol contained in the binder is such that the ratio of equivalents of hydroxyl groups to equivalents of carboxy groups is in the range of from about 0.4/1 to 1.0/1; more preferably from about 0.6/1 to 0.8/1; and most preferably from about 0.65/1 to 0.75/1.

[0020] It is further preferred that the molecular weight of the polycarboxy polymer is less than 10,000, more preferably less than 5000, and most preferably around 3000 or less, with around 2000 being most advantageous.

[0021] The use of such a low molecular weight polycarboxy polymer in the binder with the required high hydroxyl/carboxy ratio, results in a binder which exhibits few, if any, processing difficulties when preparing a fiberglass product. Sticking and balling of the fiberglass fibers during the preparation of the fiberglass mat become of minimal concern. The

The formaldehyde-free curable aqueous binder composition may be prepared by admixing the polyacid, the phosphorous-containing accelerator using conventional mixing techniques. In another embodiment, a carboxyl- or anhydride-containing addition polymer and a polyol may be present in the same addition polymer, which addition polymer would contain both carboxyl, anhydride, or salts thereof functionality and hydroxyl functionality. In another embodiment, the salts of the carboxy-group are salts of functional alkanolamines with at least two hydroxyl groups such as, for example, diethanolamine, triethanolamine, dipropanolamine, and di-isopropanolamine. In an additional embodiment the polyol and the phosphorous-containing accelerator may be present in the same addition polymer, which addition polymer may be mixed with a polyacid. In yet another embodiment the carboxyl- or anhydride-containing addition polymer, the polyol, and the phosphorous-containing accelerator may be present in the same addition polymer. Other embodiments will be apparent to one skilled in the art. As disclosed herein-above, the carboxyl groups of the polyacid may be neutralized to an extent of less than about 35% with a fixed base before, during, or after the mixing to provide the aqueous composition. Neutralization may be partially effected during the formation of the polyacid.

[0030] The formaldehyde-free curable aqueous composition may be applied to a nonwoven by conventional techniques such as, for example, air or airless spraying, padding, saturating, roll coating, curtain coating, beater deposition, coagulation, or the like.

[0031] The waterborne formaldehyde-free composition, after it is applied to a nonwoven, is heated to effect drying and curing. The duration and temperature of heating will affect the rate of drying, processability and handleability, and property development of the treated substrate. Heat treatment at about 120°C, to about 400°C, for a period of time between about 3 seconds to about 15 minutes may be carried out; treatment at about 150°C, to about 250°C, is preferred. The drying and curing functions may be effected in two or more distinct steps, if desired. For example, the composition may be first heated at a temperature and for a time sufficient to substantially dry but not to substantially cure the composition and then heated for a second time at a higher temperature and/or for a longer period of time to effect curing. Such a procedure, referred to as "B-staging", may be used to provide binder-treated nonwoven, for example, in roll form, which may at a later stage be cured, with or without forming or molding into a particular configuration, concurrent with the curing process.

[0032] More particularly, in the preparation of fiberglass insulation products, the products can be prepared using conventional techniques. As is well known, a porous mat of fibrous glass can be produced by fiberizing molten glass and immediately forming a fibrous glass mat on a moving conveyor.

[0033] The mat is then conveyed to and through a curing oven wherein heated air is passed through the mat to cure the resin. The mat is slightly compressed to give the finished product a predetermined thickness and surface finish. Typically, the curing oven is operated at a temperature from about 150°C to about 325°C. Preferably, the temperature ranges from about 180° to about 250°C. Generally, the mat resides within the oven for a period of time from about ½ minute to about 3 minutes. For the manufacture of conventional thermal or acoustical insulation products, the time ranges from about 1 minute to about 2½ minutes. The fibrous glass, having a cured, rigid binder matrix, emerges from the oven in the form of a bat which may be compressed for packaging and shipping and which will thereafter substantially recover its vertical dimension when unconstrained.

[0034] The heat-resistant nonwovens may be used for applications such as, for example, insulation batts or rolls, as reinforcing or insulation mat for roofing or flooring applications, as roving, as microglass-based substrate for printed circuit boards or battery separators, as filter stock, as tape stock, as tack board for office petitions, in duct liners or duct board, and as reinforcement scrim in cementitious and non-cementitious coatings for masonry.

#### EXAMPLE

[0035] A list of resins applied and their properties is shown in Table 1. The resins were inline mixed with a solution containing a yellow dye and an appropriate quantity of an amino silane (Osi A1101), and a soft water stream. These components were then delivered to six sets of twelve spraying nozzles where they were hydraulically dispersed. The nozzles were arranged in six circles spraying the binders towards the center of the freshly formed fiberglass from a distance of about 8 inches. The fiberglass was manufactured using a standard fiberglass spinning machine located approximately 12 inches above each circle of nozzles. The fiberglass production and binder spray rates were kept constant such that the final cured binder content represented about 5.5 weight % of the finished product. Of that cured binder content approximately 0.2% represented the silane. The final solids content of the binders as sprayed was around 10%.

[0036] Mat moistures at the exit of the forming chamber were measured for each set point (Table 2). This gives a gauge of the dry down rate of each binder. High ramp moisture has been linked to improved product performance.

[0037] Binder flow was increased until some signs of under-cure showed up and then slightly reduced. Ramp moistures were measured in excess of 5% when problems were encountered.

[0038] The recoveries and droops for each of the samples were analyzed with a two tailed t-test in which early set

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points were compared to the early control and later set points were compared to the later control. The controls were also compared to determine whether any changes had occurred during the day. Where a significant difference exists (95% confidence), it is indicated with a plus or minus. The results are shown in Table 3.

[0039] Generally, there are no significant differences in recovery or droop between TEA levels on the lower level product. Upper level recoveries and droops indicate better product performance with the higher TEA level for both resins B and D. In theory, the shorter polymer chains require more crosslinks to achieve the same mechanical properties as longer chain polymers with fewer crosslinks. Laboratory studies of crosslinker stoichiometry vs. mechanical strength of the binder indicate this to be true. A crosslinker level of approximately 70% should be used with these low molecular weight acrylic resins.

[0040] From the results, it can be concluded that building insulation can be produced with acrylic resins that are essentially emission free and formaldehyde free. This product can be produced to meet recovery specifications and have equal or better droop than standard phenolic product.

[0041] Within the family of acrylic resins (available from Rohm and Haas) the lower molecular weights present fewer processing difficulties. Collection box fiber accumulation is reduced with these acrylic variants. High binder flow rates are still beneficial to product performance. Material handling and pumping of the low molecular weight products are improved over resin A (10,000 Daltons M.W), especially in cold weather. The lowest molecular weight resin (resin D) with higher TEA stoichiometry (70%) gave the best acrylic bonded product performance (recovery and droop).

Table 1

Resin Properties				
Resin	% Solids	Molecular Weight	TEA Stoichiometry	Viscosity (25°C, 40%)
A	40%	10000 Daltons	45%	240 cP
B	51%	4500 Daltons	45%	100 cP
C	45%	3500 Daltons	45%	60 cP
D	41%	2100 Daltons	55%	20 cP
Phenolic	48%	1000 Daltons	NA	4 cP

Table 2

Let-Down Ramp Moistures				
Sample No.	1	2	3	Average
Test Point	% Moisture	% Moisture	% Moisture	% Moisture
0	2.82%	2.79%	2.32%	2.64%
X1	0.89%	0.90%	0.89%	0.89%
X2	2.03%	2.41%	1.60%	2.01%
X2B	5.74%	8.08%	3.20%	5.67%
X4	2.56%	3.51%	2.15%	2.74%
X3	1.84%	3.03%	2.18%	2.35%
X5	4.41%	5.97%	3.20%	4.53%
X7	4.42%	2.88%	4.01%	3.77%
X8	3.83%	3.92%	2.79%	3.51%
X11	2.52%	2.75%	1.77%	2.35%
T1	7.04%	6.59%	9.72%	7.78%
T2A	5.86%	6.96%	10.24%	7.69%

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**Table 2 (continued)**

Let-Down Ramp Moistures				
Sample No.	1	2	3	Average
Test Point	% Moisture	% Moisture	% Moisture	% Moisture
T2B	4.10%	4.73%	5.33%	4.72%

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Table 3. Product Performance Data

Product Performance Results		Quick		Upper level droop		Lower level recovery		Lower level droop	
	retroint		upper level recovery		upper level droop		lower level recovery		lower level droop
Binder	X1		7.44	0	2.73	0	7.02	0	1.98
Phenolic Control	X11		7.25	-	3.08	0	6.83	-	2.67
Phenolic Control	X2		6.48	-	2.68	0	6.22	0	2.56
Resin D/551 TPA	X28		6.88	-	1.53	-	6.96	0	2.02
Resin D/552 TPA	X3		6.89	-	1.71	-	7.00	0	1.98
Resin D/701 TPA	X4		6.93	-	1.60	-	6.93	0	1.73
Resin D/551 TPA/pH-3.2	X5		6.93	-	2.00	-	6.94	-	1.94
Resin C/451 TPA	X7		7.08	0	1.86	-	6.93	0	1.94
Resin B/451 TPA	X8		7.13	-	1.65	-	6.92	0	2.10

		testpoint	One Week upper level recovery	upper level drop	lower level recovery	lower level drop
Binder						
Phenolic Control		X1	7.21	3.62	6.21	3.05
Phenolic Control		X11	6.82	3.84	6.57	3.96
Resin D/551 TPA		X2	6.52	3.14	6.60	3.79
Resin D/551 TPA		X2B	6.34	2.73	6.55	2.51
Resin D/701 TPA		X3	6.67	2.14	6.28	3.42
Resin D/551 TPA/SH-3.2		X4	6.67	2.40	6.53	2.54
Resin C/451 TPA		X5	6.54	2.68	6.19	3.95
Resin B/451 TPA		X7	6.48	2.94	6.42	3.12
Resin B/701 TPA		X8	6.78	2.30	6.51	3.29

			One Month						
	Bladder	setpoint	upper level recovery	upper level droop	lower level recovery	lower level droop			
	Phenolic Control	X1	7.03	3.97	6.86	3.17	0		
	Phenolic Control	X11	6.84	4.31	6.39	4.77	-		
	Resin D/533 TPA	X2	6.12	4.52	6.39	4.37	-		
	Resin D/533 TPA	X2B	6.09	3.18	6.37	3.21	-		0
	Resin D/704 TPA	X3	6.32	3.24	6.55	3.64	-		-
	Resin D/533 TPA/DB-3.2	X4	6.42	2.68	6.49	2.96	-		0
	Resin C/433 TPA	X5	6.35	3.46	6.33	3.95	-		-
	Resin B/433 TPA	X7	6.25	3.40	6.45	3.31	0		-
	Resin B/704 TPA	X8	6.30	2.82	6.38	3.83	-		0



		antipoint	Three Month	upper level recovery	upper level drop	lower level recovery	lower level drop	
Binder		X1	7.05		3.47	6.67	0	3.30
Phenolic Control		X11	6.65		5.26	6.38	-	5.08
Phenolic Control		X2	6.25		4.51	6.47	-	5.19
Resin D/551 TEA		X2B	5.96		4.60	6.22	-	4.27
Resin D/551 TEA		X3	6.23		3.40	6.25	-	4.71
Resin D/551 TEA/PH-3.2		X4	6.32		3.03	6.30	-	3.66
Resin C/451 TEA		X5	6.29		3.91	6.20	-	4.00
Resin B/451 TEA		X7	6.23		3.75	6.29	0	4.04
Resin B/701 TEA		X8	6.16		3.33	6.01	-	5.14

\*0.0 - stand for better, same, worse than control respectively (95% confidence), all measurements are in inches

[0042] While the invention has been described with preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to

be considered within the purview and the scope of the claims appended hereto.

# Claims

- 5 1. A fiberglass binder, comprising an aqueous solution of
  - a) a polycarboxy polymer,
  - b) a polyol,
- 10 with the amount of polycarboxy polymer and polyol in the binder being such that the ratio of equivalents of hydroxyl groups to equivalents of carboxy groups is in the range of from about 0.4/1 to 1.0/1.
2. The fiberglass binder of claim 1, wherein the molecular weight of the polycarboxy polymer is 10,000 or less.
- 15 3. The fiberglass binder of claim 2, wherein the binder further comprises a catalyst comprising an alkali metal salt of a phosphorus containing organic acid.
4. The fiberglass binder of claim 2, wherein the molecular weight of the polycarboxy polymer is about 5000 or less.
- 20 5. The fiberglass binder of claim 2, wherein the molecular weight of the fiberglass binder is about 3000 or less.
6. The fiberglass binder of claim 3, wherein the catalyst is comprised of sodium hypophosphite, sodium phosphite or mixtures thereof.
- 25 7. The fiberglass binder of claim 2, wherein the polyol is triethanolamine.
8. The fiberglass binder of claim 1, wherein the polycarboxy polymer comprises a homopolymer or copolymer of polyacrylic acid.
- 30 9. The fiberglass binder of claim 4, wherein the amount of polycarboxy polymer and polyol are such that the ratio of equivalents of hydroxyl group to equivalents of carboxy group is in the range of from about 0.6/1 to about 0.8/1.
10. The fiberglass binder of claim 9, wherein the ratio is in the range of from about 0.6/1 to about 0.75/1.
- 35 11. The fiberglass binder of claim 5, wherein the ratio of equivalents of hydroxyl group to equivalents of carboxy group is in the range of from about 0.65/1 to about 0.75/1.
12. A fiberglass binder, comprising an aqueous solution of
  - 40 a polycarboxy polymer which comprises a homopolymer or copolymer of polyacrylic acid, and with the molecular weight of the polyacrylic acid being about 5000 or less, triethanolamine, and
  - a catalyst comprised of sodium hypophosphite, sodium phosphite, or mixtures thereof,
  - 45 with the amount of the polyacrylic acid and triethanolamine being such that the ratio of hydroxyl group to carboxyl group equivalents is in the range of from about 0.65/1 to 0.75/1.
13. The fiberglass binder of claim 12, wherein the molecular weight of the polycarboxy polymer is about 3000 or less.
14. The fiberglass binder of claim 12, wherein the molecular weight of the polycarboxy polymer is about 2000.
- 50 15. A fiberglass product comprising a mat of glass fibers containing the binder of claim 1.
16. A fiberglass product comprising a mat of glass fibers containing the binder of claim 12.
- 55 17. The fiberglass product of claim 15, wherein the product is building insulation.
18. The fiberglass product of claim 15, wherein the building insulation is insulation for the roof.

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19. The fiberglass product of claim 16, wherein the product is building insulation.

20. A process for making a fiberglass fiber mat using a binder, with the binder comprising the fiberglass binder of claim 1.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 99 11 6458

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X,D	US 5 661 213 A (ARKENS CHARLES THOMAS ET AL) 26 August 1997 (1997-08-26) * column 4, line 21 - line 31; claims; example 18; table 14.1 *	1-20	D04H1/64 C08F8/14
D,X	US 5 318 990 A (STRAUSS CARL R) 7 June 1994 (1994-06-07) * column 2, line 57 - column 3, line 21; examples 3,4; table I * * column 3, line 22 - line 52 *	1-20	
X	EP 0 651 088 A (ROHM & HAAS) 3 May 1995 (1995-05-03) * examples 9,11,14 * * page 5, line 9 - line 29; claims 1,2 *	1-3,6-8, 15,17-20	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			D04H C08F
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>31 January 2000</b>	Examiner <b>Barathe, R</b>
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
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31-01-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5661213 A	26-08-1997	AT 160597 T	15-12-1997
		AU 667921 B	18-04-1996
		AU 4212793 A	28-04-1994
		BR 9303315 A	22-03-1994
		CA 2101450 A	07-02-1994
		CN 1083844 A	16-03-1994
		CZ 9301592 A	16-03-1994
		DE 69315393 D	08-01-1998
		DE 69315393 T	30-04-1998
		DK 583086 T	02-02-1998
		EP 0583086 A	16-02-1994
		ES 2109441 T	16-01-1998
		FI 933473 A	07-02-1994
		GR 3026182 T	29-05-1998
		HK 1001096 A	22-05-1998
		HU 66516 A	28-12-1994
		IL 106446 A	30-09-1997
		JP 6184285 A	05-07-1994
		MX 9304685 A	31-03-1994
		NZ 248215 A	26-09-1995
		SK 82993 A	06-04-1994
		US 5763524 A	09-06-1998
		ZA 9305397 A	07-02-1994
US 5318990 A	07-06-1994	NONE	
EP 0651088 A	03-05-1995	US 5427587 A	27-06-1995
		AU 694136 B	16-07-1998
		AU 7594694 A	11-05-1995
		BR 9404180 A	27-06-1995
		CA 2118298 A	23-04-1995
		CN 1109931 A	11-10-1995
		FI 944955 A	23-04-1995
		JP 7189131 A	25-07-1995
		US 5718728 A	17-02-1998

EPO FORM P049

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82